

# **Molecular Engineering for Gas Purification**

## **Monthly Report for February 2003-March 2003**

### **Task 1: Reporting (10/1/02-9/31/03) \$ 10K BNL**

The PI will provide a monthly report on the progress and activity during the month. The monthly report should not be longer than 2-3 pages and should not take more than 2-3 hours per month to accomplish. This report will summarize the activity on this project for the subject month for each task and will contain monthly and cumulative costs and time expended on the project for each task. A plot of estimated and project costs shall be submitted with the monthly report.

### **Task 2: Set Logistics of Procedure and Experimental Approach (10/1/02-12/31/02) \$ 40K; BNL/VCU**

**Subtask 2.1:** The team will get together and make plans for experiments (purchasing parts and supplies).

**Accomplishment:** In addition to communication by e-mail, fax and telephone, the BNL and VCU teams have visited each other to acquaint the members with the space and equipment. As the study progresses these visits will become more frequent as the members use the other's equipment and expertise.

**Subtask 2.2:** The team will set up, modify and calibrate the imprinting instruments for processing small gases.

**Accomplishment:** We have set up a tentative experiment protocol, which will involve many trial and error tests. The protocol is subject to change pending the outcome of the subsequent tests.

1. The experiment will be initiated with modification and calibration of existing equipment.
2. A syringe pump will be used to pressurize the solvent/substrate mixture to supercritical pressures at controlled temperatures. The concentrations, pressure and temperature of the process will be systematically studied to define the supercritical states. Initially the phase diagram of common solvents i.e. CO<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> will serve as guidelines.
3. The mixture will be sprayed onto the surface of a solid support. The rate of expansion, distance, temperature and pressure will be systematically varied to achieve a coating that ranges from micro to nanometer on the surface, a factor that affects the permeability and durability of the coating. Many tests will be needed to optimize the performance of the coating formed.
4. The coating will be imprinted with the template molecules by using UV light to polymerize the coating with the template in place. The concentration of template molecule will be systematically changed to study their effect on the properties of the formed coating.
5. The template will be removed from the polymerized surface under reduced pressure and then tested for molecular selectivity. The product will be analyzed with SAW, electron microscopy and FTIR spectroscopy for surface structure studies.

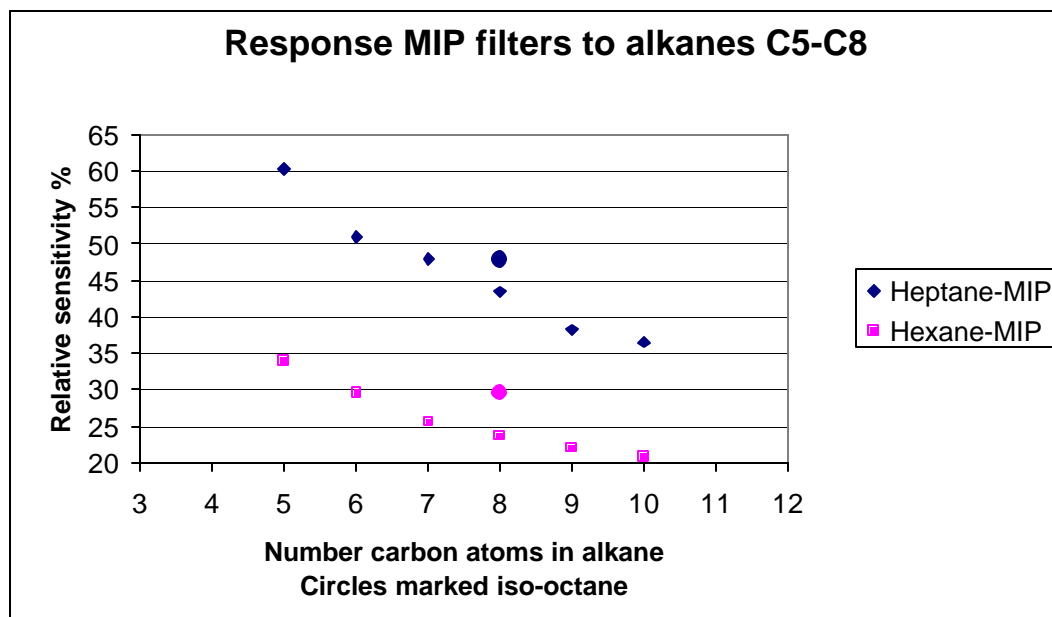
### **Task 3: Develop Selectivity Polymers Against C<sub>5</sub>-C<sub>6</sub> (1/01-2/28/03) \$ 50K; BNL/VCU**

**Subtask 3.1:** Conduct polymerization with n-pentane, isopentane, n-hexane, and hexane isomers as templates and test for selectivity and durability against C<sub>5</sub>-C<sub>6</sub> condensable hydrocarbons.

**Accomplishment:** Higher hydrocarbons such as hexanes C6 and heptanes C7 consist of a small percentage (up to 1%) in natural gases which need to be removed in the production of natural gas. We used hexane as the template vapor in an attempt to reduce the pore size and, correspondingly, increase the efficiency of the polymer material for separating C5 to C8 from small molecules. The ultimate project goal is to extend this work to very small molecules such as methane.

The following figure is a plot of the relative sensitivity of both heptane and hexane imprinted polymers (with respect to an unimprinted control) as a function of alkane size from C5 to C8. As can be seen in the figure, for both templates the vapor affinity decreases as the size of the alkane molecule is increased. Furthermore, the hexane-imprinted materials, as expected, exhibit a lower affinity to all alkanes in comparison to the heptane-imprinted material. This is strong evidence that we are successfully reducing the material porosity by reducing the size of the template vapor.

There are many processing variables that must be investigated before the process can be optimized and extended to smaller template vapors. This will be reported in next task.



Subtask 3.2: Optimize the reaction conditions including concentration of template, thickness of polymer, and reaction parameters such as temperature, pressure and UV irradiation time.

#### **Accomplishment:**

We intend to develop polymeric materials with controlled nanoscale porosity for selective gas separation applications. The process involves supercritical fluid precipitation of a solid-state linear monomer followed by vapor treatment and UV photopolymerization. The resulting polymer shown in subtask 3.1 exhibits a nanoscale porosity that is characteristic of the vapor used during the process. The optimization of the reaction conditions including concentration of template, thickness of polymer, and reaction parameters such as temperature, pressure and UV irradiation time is shown in the following Table 1. We found that the more crystalline DSP monomer exhibits extremely complicated recrystallization kinetics, while the EPA monomer is more predictable.

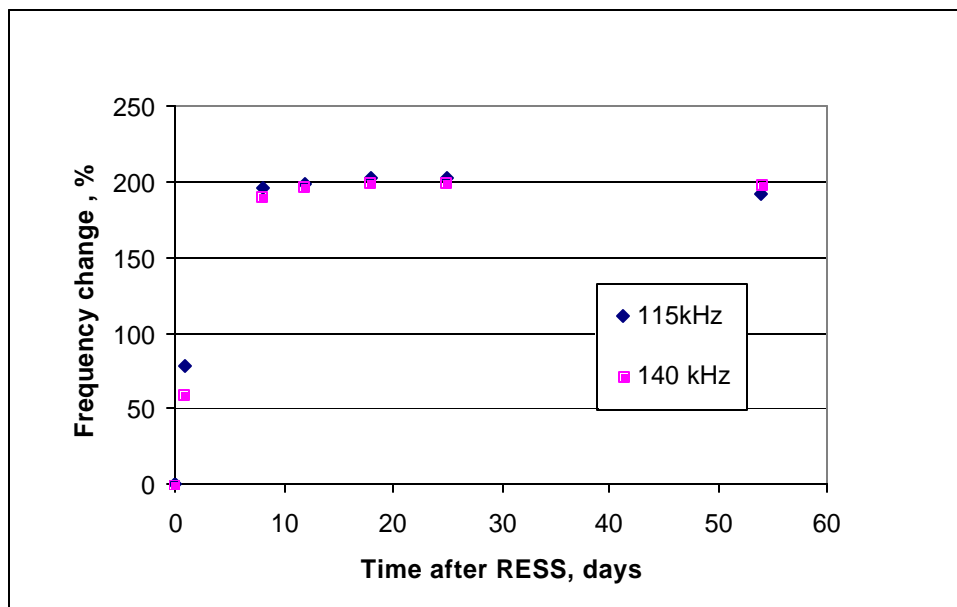
Table 1. PARAMETERS INVESTIGATED

Parameter	Range	Notes
<b><i>RESS conditions</i></b> Preexpansion temperature Preexpansion pressure	125 °C, 130°C, 150°C 5000 psi, 7000 psi	Particles development
<b><i>Monomer age before MIP</i></b> (time after RESS precipitation before the start of MIP procedure)	30 min, 60 min, 90 min, 150 min, 1 week, 2 weeks	Recrystallization
<b><i>Vapor sorption time</i></b>	10 min, 15 min, 60 min, 80 min, 90 min, 100 min,	Recrystallization
<b><i>Template carrier gas</i></b>	Oxygen present (Air) Oxygen absent (Nitrogen)	Recrystallization
<b><i>Template concentration</i></b>	Saturated vapor pressure Below saturated (diluted)	Recrystallization
<b><i>UV irradiation time</i></b>	10 min, 15 min	Polymerization
<b><i>UV spectral range</i></b>	228-600 nm with maximum at 228-450 nm; PS filter cut of wavelength shorter than 310 nm	Polymerization

Subtask 3.3: Analyze the imprinted polymers by Atomic Force Microscope (AFM), Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM).

#### Accomplishment:

Product analysis using electron microscopes is in progress. The polymeric products made from DSP monomer were analyzed by using Surface Acoustic Wave (SAW) as shown in Figure 1.



**Figure 1.** DSP monomer particles change as studied by the SAW devices

Figure 1 shows the changes in DSP monomer tracked by the change in the frequency of the DSP coated SAW transducer. The RESS conditions were: preexpansion temperature and pressure of 128-126 °C and 5000 psi respectively (10-16-02). As can be seen from the picture, the major changes in the DSP particles occurred in the first days with no notable changes after 12 days. The kinetics of frequency change of the DSP coated SAW device in the first 24 hours is extremely fast. EPA particles shown in Figure 2 were developed at preexpansion temperature and pressure of 126 °C and 5000 psi respectively.

**Task 4: Develop Selectivity Polymers Against C<sub>3</sub>-C<sub>4</sub> (3/1-4/30/03) \$ 40K; BNL/VCU**

**Subtask 4.1:** Conduct polymerization with n-butane, n-propane and isopropane as templates and test for selectivity and durability against C<sub>3</sub>-C<sub>4</sub> hydrocarbons.

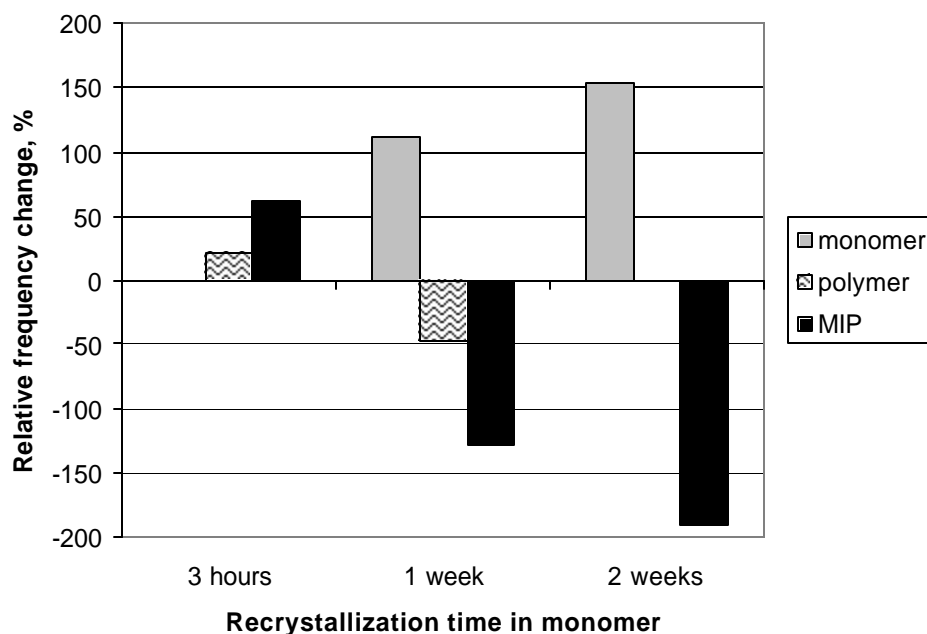
In progress

**Subtask 4.2:** The team will optimize the reaction conditions including concentration of template and monomer and reaction conditions including temperature, pressure and UV irradiation time.

**Accomplishment:**

During this reporting period we continued our process optimization studies. In particular, the monomer recrystallization kinetics was investigated. The imprinting process relies on the following sequence of processing steps: 1) amorphous nanoparticle formation by RESS, 2) vapor induced recrystallization, 3) photopolymerization and 4) vapor extraction. The naturally crystalline monomer material is formed in a metastable amorphous state by the rapid precipitation process. The amorphous particles are then recrystallized through exposure to a template vapor. However, we found that the particles will also recrystallize on their own even without vapor exposure, but at a much slower rate. Therefore, we believe that the imprinting process strongly depends on the timing of the sequence. In particular, the time delay between steps 1 and 2 in the above sequence is expected to significantly influence the final product morphology. We investigated the influence of the DSP monomer recrystallization time (time after development) on both imprinted and non-imprinted particles (i.e. with and without vapor treatment). Heptane was used as the template vapor. The MIP conditions were: 90 minutes of sorption and polymerization conditions were: 10 minutes of UV polymerization under dry nitrogen. DSP monomer nano particles were developed by RESS and were polymerized the same day, 1 week after RESS and 2 weeks after RESS in presence of template as well as without vapor treatment.

As we reported earlier, SAW devices coated with DSP monomer particles show significant frequency change (up to 200 %) during the first two weeks with no substantial frequency change after 2 weeks. We believe that the observed frequency change is caused by the DSP recrystallization and, therefore, estimate that the natural (i.e. without vapor exposure) recrystallization time is about 2 weeks. Fig.1 depicts the SAW frequency change (related to the initial monomer loading during RESS) due to monomer age and the polymerization or MIP process.



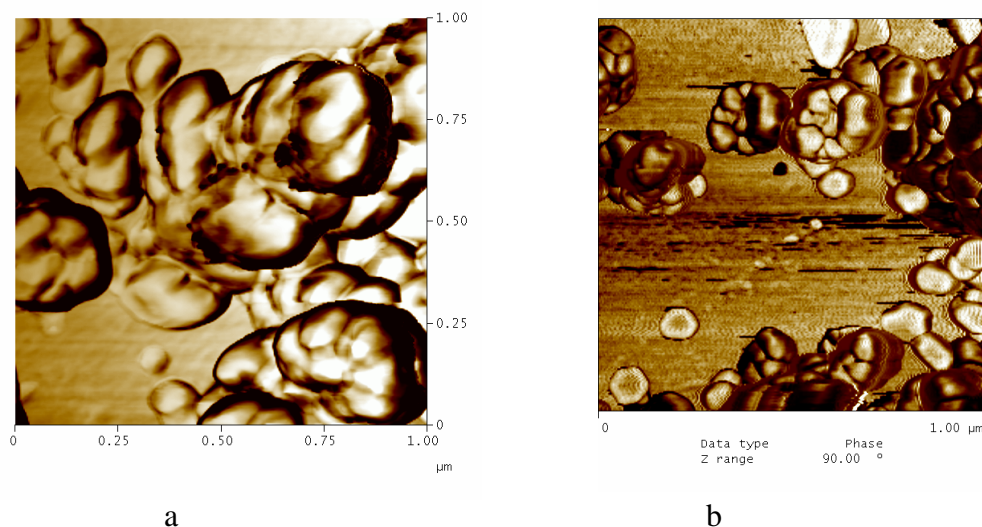
**Figure 1.** The frequency change due to polymerization and vapor treatment and polymerization (MIP)

Several trends can be observed. For the monomer, we observe the expected frequency increase during the first two weeks. Despite this, polymerization (polymer) or imprinting and polymerization (MIP) cancels out the frequency gain and reverses the trend if the monomer age is longer than 1 week. One possible explanation for the observed trends shown in figure 1 is the effect of the underlying natural recrystallization process. The change in SAW frequency depicted in Fig.1 reflects the changes in the physical properties of the DSP particles, rather than a mass change. The SAW resonance frequency depends not only on the mass of the coating, but also on the physical properties of the coating material (stiffness, viscoelasticity, plastification), and the adhesion of the coating to the transducer surface. The frequency increase observed for the DSP monomer is assigned to rearrangements of the amorphous particles to more defined structures.

**Subtask 4.3:** Analyze the imprinted polymers by Atomic Force Microscope (AFM), Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) for surface analysis and infrared spectroscopy for cross-linking analysis. Study structure and selectivity relationship.

#### **Accomplishment:**

An AFM study reveals the difference in DSP polymer particles polymerized immediately (within hours) after RESS and after 1 week of natural recrystallization in the dark. Fig.2 shows AFM phase images of DSP polymer particles polymerized without vapor treatment in 2 hours and after a 1week after development.



**Figure 2.** AFM phase images of DSP particles polymerized immediately after RESS (a) and after 1 week recrystallization in monomer (b).

It can be seen in the images of figure 2 that the shape and morphology of the DSP particles have changed after one week of monomer storage. The original RESS particles have a rounded shape with no well defined boundaries between individual particles within the clusters. After 1 week the individual particles become well separated and their shape changes from rounded to more edge defined, which suggests recrystallization. This trend becomes even more pronounced for the vapor-treated DSP particles (not shown). A sensitivity study towards alkanes showed a difference as well. Fig.3 shows the overall sensitivity to the heptane template as a function of the time between particle formation and photopolymerization both with and without a template vapor. As can be seen in the figure, the sensitivity increases with time with the imprinted particles exhibiting higher sensitivity in comparison to the control (photopolymerized without template).

**Task 5: Develop Selectivity Polymers Against Short Straight Chain Gases (5/1-6/30/03) \$ 50K; BNL/VCU**

Subtask 5.1: Conduct polymerization with methane, ethane, CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>S as templates and test for selectivity and durability against these contaminating gases.

Subtask 5.2: Test selectivity and durability of the imprinted polymer against a representative raw natural gas and a low quality natural gas.

**Task 6: Study the Structure and Selectivity Relationship for Improving the imprinting Process and Product. (7/1-9/30/03); \$ 50K; BNL/VCU**

Subtask 6.1: Design processes to incorporate the imprinted polymer onto solid supports.

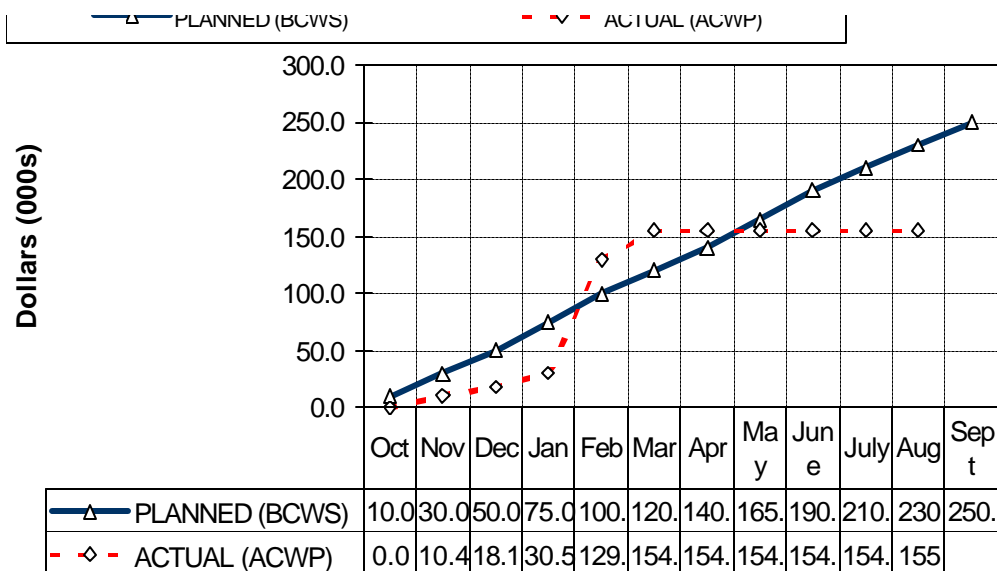
Subtask 6.2: Initiate the fabrication of working units using imprinted polymer with supports in the form of membrane or sieve.

**Task 7: Annual Progress Report** (9/1-9/30/03); \$ 10K; BNL/VCU

An annual report will be generated and submitted to DOE/NETL Gas Program Project manager for this project. The report will be a thorough accounting of all effort and findings as a result of this funded research. The report will contain a section detailing the cost and level of this project for the subject year.

**Significant Issues and Corrective Action**

None



(\$K)	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	FY02
Planned Cost	10.0	20.0	20.0	25.0	25.0	20.0	20.0	25.0	25.0	20.0	20.0	20.0	250.0
Actual Cost	0.0	10.4	7.8	12.4	98.8	25.0							
Variance Cost	10.0	9.6	12.2	12.6	-73.8	-5.0	20.0	25.0	25.0	20.0	20.0	20.0	
Cumulative Planned	10.0	30.0	50.0	75.0	100.0	120.0	140.0	165.0	190.0	210.0	230.0	250.0	250.0
Cumulative Actual	0.0	10.4	18.1	30.5	129.3	154.9	154.9	154.9	154.9	154.9	155.0		
Cumulative Variance	0.0	9.6	21.9	34.5	-39.3	-44.3	-24.3	0.7	25.7	45.7	65.7		

Milestones	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	FY03
1) Monthly Reports to John Rogers (NETL)	☆	☆	☆	☆	☆	☆	△	△	△	△	△	△	
2) Set logistics of procedure and experimental approach			☆										
3) Develop selectivity polymers DSP against C5-C6				☆									
4) Develop selectivity polymers against C3-C4					☆								
5) DSP against short straight chain gases						☆							
6) Study structure/selectivity relationship							△						
7) Annual Prpgress Report												△	

LEGEND	SCHEDULED	△	DEVIATION	□	COMPLETED	☆
	TIME LINE	—	ELIMINATED BY REDUCTION	⊗		

## Schedule and Cost Variances

Funding arrived BNL in late September 2002. Soon, an account was set up in October and work started in October. The schedule and milestone were delayed by two months from the FWP submitted. Also due to a delay in subcontracting process to Virginia Commonwealth University, the fund has not been forwarded to VCU. Therefore, there is small cost variance in starting the program as shown in the following chart and table.